On the Spectrum of Silicon; with a Note on the Spectrum of Fluorine.

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(Communicated by Sir David Gill, K.C.B., F.R.S., H.M. Astronomer at the Cape of Good Hope. Received February 13,—Read March 2, 1905.)

(PLATE 2.)

In a recent paper* M. A. de Gramont questions the silicon origin of certain lines, viz.: λ 4089·1, λ 4096·9, and λ 4116·4, grouped together as Group IV by Sir Norman Lockyer† who ascribes them to the element named. He says: "J'ajouterai que les lignes du groupe IV, qui indiqueraient, d'après Lockyer, une température excessive, ont toujours, sur mes clichés, accompagné les raies de l'air et ont disparu avec lui. Elles coïncident avec des lignes de l'oxygène et de l'azote, et ces deux gaz ont été reconnus dans plusieurs étoiles d'Orion et dans *β Crucis*. Je crois donc le groupe IV attribuable à l'air."

Sir Norman Lockyer and Mr. Baxandall‡ have replied by bringing forward photographic evidence in support of their conclusions. Whilst agreeing with the latter authors that the lines in question, *with the exception of* λ 4096·9, are really silicon lines, I consider that the evidence brought forward by them is in itself insufficient to establish their conclusions satisfactorily.

Nearly three years ago I prepared a paper, "On the Spectrum of Silicon from its dissociated compounds," for inclusion in vol. 10 of the 'Annals of the Cape Observatory,' but as this volume has not yet appeared, owing to other papers being still under preparation, it seems desirable to publish, in advance, an extract dealing particularly with the lines under present discussion and to mention briefly some other important lines. The extract is as follows:—

"*High-temperature lines* λλ 4089·1 *and* 4116·4.

"These two lines were first recorded as silicon lines by Lockyer in his 'Note on the Spectrum of Silicon,'§ and it is of great interest to notice their behaviour under different conditions. Of these lines Lockyer writes, 'The

* 'Comptes Rendus,' vol. 139, p. 188.
† 'Roy. Soc. Proc.,' vol. 67, 1900, p. 405.
‡ 'Roy. Soc. Proc.,' vol. 74, 1904, p. 296.
§ 'Roy. Soc. Proc.,' vol. 65, p. 449.

lines in Group IV* have never been seen in the spark spectrum of silicium when small coil and small jar capacity are used,† but with the spark given by the Spottiswoode coil and plate condenser, they appear as weak lines. They are not, like the members of Groups II and III seen in the spectrum from the bulb when a vacuum tube is used, but in that given by the capillary the strongest ones are very prominent, and vie in intensity with the lines in Group III.'

"At the outset it may be stated that a large number of experiments had to be made before the confirmation of the silicon origin of these lines was considered satisfactory, but there can now be no doubt that Lockyer's identification is correct. These lines are absent in the list of lines given by Exner and Haschek, and by Eder and Valenta, and, so far as I know, no other observers have recorded them.

"In my earlier experiments with argon tubes‡ I had obtained these lines from the glass capillary, not only of argon tubes but also from those of other tubes containing various gases; and concluded that they may be obtained from glass vacuum tubes, whatever the gaseous contents may be, provided that sufficient jar capacity and a suitable spark gap are employed to decompose the glass. That I then doubted their silicon origin, however, is shown by the fact that they were not included in the list of silicon lines discussed in my first paper. This was owing to the fact that the spark spectrum of silicon tetra-fluoride had only been examined in wide tubes at atmospheric pressure, under which conditions the lines in question are absent, unless the immediate vicinity of the platinum electrodes is examined.

"I find that even at a pressure of 12·5 mm. the glass capillary of a silicon tetra-fluoride tube fails to give these lines when a small jar and gap are used, although the other silicon lines are very pronounced. If, however, the pressure be reduced to 3 mm., still using one small jar and gap, these lines come out strongly and are almost as strong as the strongest lines in the whole spectrum. With a similar pressure of silicon tetra-chloride, however, using the same jar and gap, these lines are exceedingly weak, whilst the rest of the silicon lines are strong.

"It is thus evident that the silicon spectrum from a mixture of silicon and chlorine (dissociated silicon tetra-chloride) is very different from that obtained from a similar mixture of silicon and fluorine (dissociated silicon

* Group IV consists of three lines, the two above, and one, λ 4096·9, which I do not obtain in my photographs, and regard its silicon origin as doubtful.

† I show later that small coil and jar capacity suffice to bring out these lines strongly in the spectrum from the capillary of tubes of the fluoride.

‡ 'Roy. Soc. Proc.,' vol. 66, p. 44.

tetra-fluoride). The effect of the chlorine being, apparently, to lower the temperature of the gas, and so extinguish the lines which require the highest temperature for their production.

"Lockyer* found that the presence of the chlorine in the dissociated chlorides of various metals had the effect of extinguishing the short, and therefore presumably high-temperature lines, for he writes: 'It was found, in all cases, that the difference between the spectrum of the chloride and the spectrum of the metal was: *That under the same spark conditions, the short lines were obliterated, while the air lines remained unchanged in thickness.* Changing the spark conditions by throwing the jar out of the circuit, this change was shown in its strongest form, the final results being that only the very longest lines in the spectrum of the metal remained.'

"This pronounced difference between the behaviour of silicon tetra-fluoride and silicon tetra-chloride had the effect of again throwing doubt on the silicon origin of the lines under discussion. On examining, however, the photographs taken for the purposes of the former paper, in which the spark spectrum had been taken in hydrogen from beads of sodium and potassium silicates made from rock-crystal, it was seen that these lines *did* occur as short lines close to the beads, but not extending throughout the spark, as did the other lines. This, in itself, was another evidence, not only of their silicon origin but also of the high temperature requisite for their production.

"All further doubt was, however, set at rest by preparing other beads of potassium silicate from carefully purified silica, made from silicic acid precipitated from silicon tetra-fluoride by water. The spectrum of these beads showed these lines as short lines as in the case of rock-crystal silicate, and their length was not much increased by sparking the beads in the fused state.

"Accordingly, the weakness or absence of these lines from the capillary of silicon tetra-chloride vacuum tubes was attributed to the above-mentioned effect of chlorine. These lines can, however, be obtained from silicon tetra-chloride tubes as strong lines, having much the same relative intensity as those obtained by Lockyer from the bromide, by increasing the number and size of jars and the width of the spark-gap; *but only at the expense of decomposing the glass of the tube itself.* This decomposition of the glass is evidenced by the appearance of a strong spectrum of oxygen and the almost complete obliteration of the chlorine spectrum, much in the same way as the spectra of argon and helium can be obliterated and replaced by those of silicon and oxygen. The spectrum thus obtained, is, in fact, practically identical with

* 'Phil. Trans.,' vol. 163 (1873), p. 258.

that obtained under similar conditions from a tube filled with pure oxygen at low pressure (2 mm.), residual air or any other gas, and cannot in any way be regarded as a spectrum of dissociated silicon tetra-chloride.

"A consideration of these facts suggests a serious objection to the acceptance of the spectrum obtained by Lockyer from a silicium bromide capillary vacuum tube by the use of the large Spottiswoode coil and plate condenser, as evidence that the lines in question are silicon lines. It is clear that they may be and probably are obtained from the glass tube and might equally well belong to some other material contained in it.

"For example, the H and K lines of calcium and the D lines of sodium, and even the strong triplet of manganese often accompany such spectra, and one might equally well attribute the lines to some other and possibly unknown substance.

"The weakness of the lines when obtained from silicon itself, a substance likely to contain impurities, as results show, and the fact that Exner and Haschek did not obtain them from the specimens of silicon with which they worked, would rather suggest that they were due to some impurity in Lockyer's specimen of silicon; the fact of obtaining them as such strong lines from a silicium bromide capillary vacuum tube, under the conditions of his experiments is no evidence to the contrary.

"Such evidence must, in fact, be obtained from carefully prepared pure silicates, or other pure silicon compounds, *sparked under such conditions that the presence of glass cannot possibly vitiate the results.* These two lines are present in ϵ Canis Majoris and other helium stars, as strong lines, together with other silicon lines, but the low-temperature silicon lines are either absent or very weak, the only low-temperature lines present in ϵ Canis Majoris being the persistent pair 4128 and 4131, which are weak and indistinct lines."

The photographs presented by Lockyer and Baxandall only serve to confirm the views expressed in the foregoing extract, viz.: that the silicon lines from their vacuum tubes filled with gaseous silicon compounds have their origin as much in the material of the glass capillary as in the gaseous compound introduced, and if we had no other evidence to the contrary, we might equally well say that the lines of calcium, sodium, and manganese, which appear in vacuum tubes so filled, belong to silicon and not to the metals named.

The spectra of silicon tetra-fluoride vacuum tubes reproduced in their paper show a very strong spectrum of oxygen, which is sufficient evidence

that the spark conditions were such as to result in the decomposition of the glass of the tube, which introduces great uncertainty as to the nature of all the materials thus rendered incandescent. The oxygen lines cannot be due to contamination with atmospheric air, as the spectrum of nitrogen is absent.

The photographs of spectra which accompany this note, show clearly the unimportant part played by the silicon tetra-fluoride in the production of the silicon lines in Lockyer and Baxandall's photographs, as their spectrum is practically identical, except for the presence of a few fluorine lines, with the second strip of the photographs sent herewith, which was produced from an oxygen tube, and could have been equally well obtained from a tube containing argon, helium or other gases under suitable conditions (Plate 2).

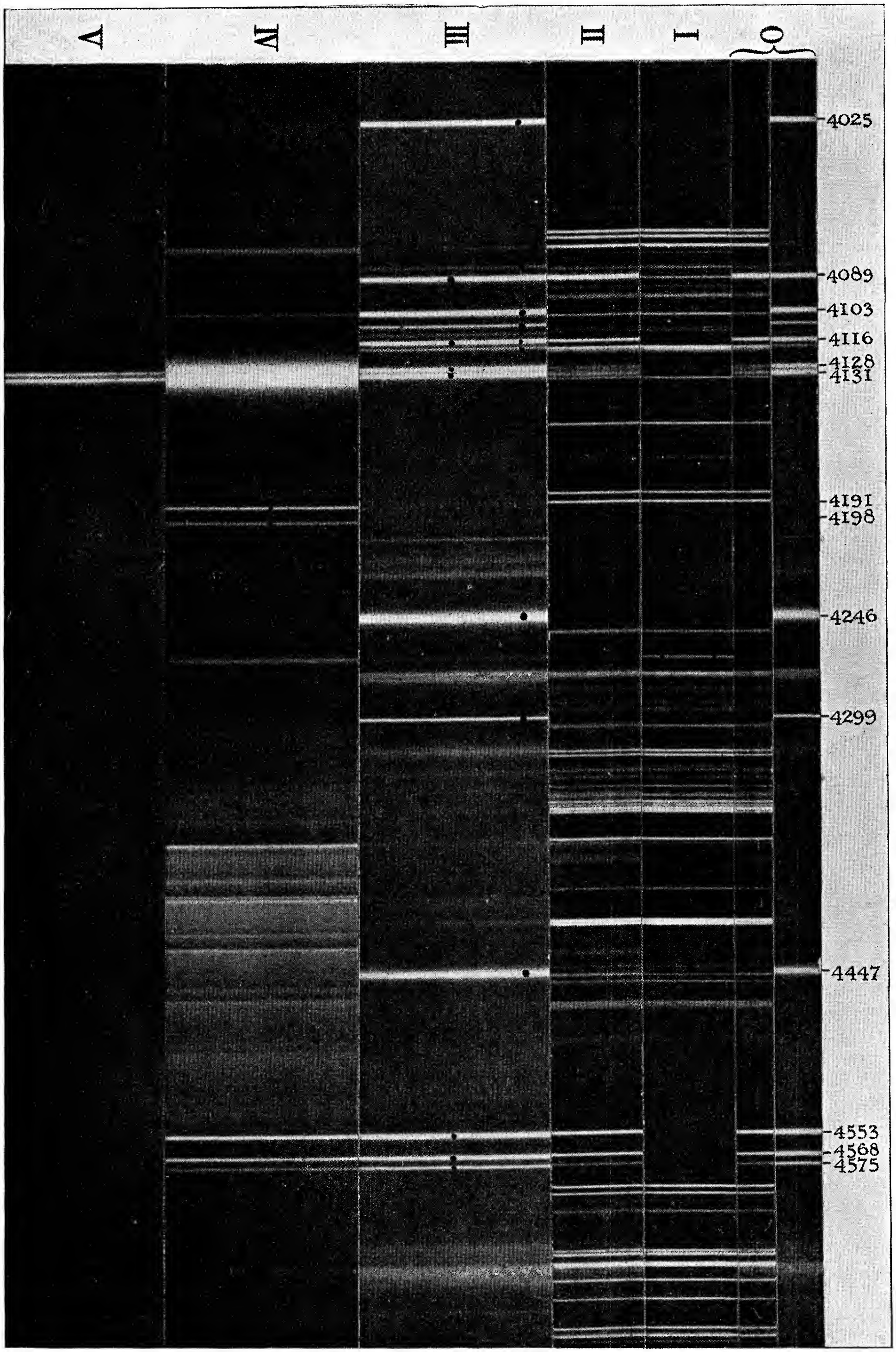
The first strip shows the spectrum of oxygen for comparison. It was taken from the same tube as the second strip, but with small coil and small jar instead of the heavy disruptive discharge from the large coil and four large jars. The third strip shows, however, that a *true* spectrum of dissociated silicon tetra-fluoride may be obtained without simultaneously producing a strong oxygen spectrum. This is a spectrum of the gaseous materials purposely introduced into the tube, and not one of the glass of the tube itself, and therefore it has far more value as evidence, especially in view of M. de Gramont's statement that the lines of Group IV, in his experiments, appear and disappear with the air lines.

This photograph was produced with a small coil and a small jar, which gave a discharge insufficient to decompose the glass capillary. It will be seen that the spectrum of oxygen is almost completely eliminated, a trace only of the strongest lines, the strong triplet mentioned by Lockyer and Baxandall, being just perceivable.

The two strong lines of Lockyer's Group IV are, however, amongst the strongest in the spectrum, and they are accompanied by the well known pair $\lambda\lambda$ 4128 and 4131 in Group II and the strong triplet of Group III. *

Moreover the spectrum of fluorine, considered later, is much stronger than in the Kensington spectra. The strongest fluorine lines are marked with one black dot at the upper end, whilst the silicon lines are marked by one black dot in the middle, the wide pair of silicon lines to the left being the two strong lines of Lockyer's Group IV, λ 4089 and λ 4116, the close pair on their right belonging to his Group II, λ 4128 and λ 4131,

* Sir Norman Lockyer and myself almost simultaneously and independently discovered these strong stellar lines (Group III) to be due to silicon, but both of us had not noticed that M. de Gramont had previously recorded them as silicon lines, which he found in the spectra of silicates ('Comptes Rendus,' vol. 124, p. 192).


V
IV
III
II
I
O
4025
4089
4103
4116
4128
4131
4191
4198
4246
4299
4447
4553
4568
4575

and the strong triplet on the right being Group III, λ 4553, λ 4568, and λ 4575.

Strip IV shows the central part of a negative taken from a silicon tetra-fluoride capillary under conditions which leave part of the SiF_4 undecomposed, as the band spectrum of this compound (mentioned also by Eberhard) shows. In this the fluorine lines are practically absent, although the silicon lines are very strong.

All the 12 lines * (Group IV being absent) of Lockyer's first three groups are exceedingly distinct, as well as two lines, the pair to the right of the very strong pair λ 4128 and λ 4131, which I regard as two new silicon lines not hitherto recorded by any who have worked on the spectrum of silicon.

Strip V shows the pair 4128, 4131 as intense as in strip III, but without the lines of Groups III and IV. It is interesting as representing the low-temperature stellar spectrum of silicon reproduced in the laboratory. It is from a silicon tetra-chloride vacuum tube.

Herr G. Eberhard † has also made an important investigation of the spectra of silicon obtained from its halogen compounds, he says: "The arc lines λ 3905 and λ 4103 occur throughout the spark, but the lines λ 4089 and λ 4116 on the contrary occur only in the immediate neighbourhood of the points of the electrodes," which agrees with the results of my experiments with silicates mentioned in the preceding extract, and probably explains why Exner and Haschek missed these lines, as Eberhard points out.

The wave-length of the silicon line 4116 cannot be accurately measured in presence of a strong fluorine spectrum unless sufficient dispersion is employed to separate the slightly less refrangible fluorine line.

I have hitherto left out of account the middle line of Lockyer's Group IV, viz.: λ 4096·9. It is a very important stellar line as the following extract from Cannon and Pickering's‡ intensities show.

	29 Can. Maj.	τ Can. Maj.	ε Orionis.	β Centauri.	γ Orionis.
4089·2§	6	12	15	5	2
4096·9	18	6	4	2	1
4101·8 H_δ	25	25	25	35	40
4116·2	3	6	10	2	0

* The green pair 5042, 5057, the arc line 3906, and the Group II triplet 3854, 3856, and 3863 are outside the limits of the strip sent for reproduction.

† 'Zeitschrift für Wissenschaftliche Photographie, Photophysik und Photochemie,' Band 1, Heft 10, 1903, p. 349.

‡ 'Annals of the Observatory of Harvard College,' vol. 28, part 2, pp. 233 and 235.

§ The first and last of these are silicon lines. Cannon and Pickering assign no origin.

They say: "4096·9 is so near H_δ wave-length 4101·8 that it gives the hydrogen line the appearance of being double, or of having a bright central line superposed on a broad dark line. By superposing this spectrum upon that of another star, it is easily seen that H_δ is not double.

"It then appears that H_δ of the superposed image matches the line of greater wave-length in this spectrum and the line 4096·9 is well separated from the hydrogen line. 4096·9 has not been seen in the preceding classes of spectra, and is strongest in spectra of this class (viz., Oe) declining in intensity in succeeding classes until B_2A is reached, when it is not present."

It is doubtless the same line that Lockyer* records as λ 4097·3 in ε Orionis, ascribing its origin to Si (IV), and Hartmann† in δ Orionis as λ 4097·49, he also ascribing it to silicon, following Lockyer and Exner and Haschek as regards origin. Exner and Haschek find its wave-length as 4096·8, whilst A. de Gramont places a line at λ 4097·3, but ascribes it to air. Eberhard does not mention any silicon line here.

This line is certainly not present in the purest silicon spectra which I have been able to obtain and which show the other two lines of Group IV strongly. In strip III of the accompanying photographs its place lies between the silicon line 4089 and the fluorine line 4103, a region destitute of lines of any kind.

In 29 Can. Maj., according to Cannon and Pickering, this line is three times as intense as the stronger silicon line of Group IV, but—as is shown in the preceding extract from their intensities—it becomes weaker in stars showing the Group IV lines of silicon more strongly. I am convinced, therefore, not only because of the absence of this line in strip III and its relative weakness in the spectra of both Lockyer and Exner and Haschek, but also because of stellar evidence, that some other origin than silicon must be sought for this line.

There are both oxygen and nitrogen lines very close to this place, but neither of these elements account for the strong stellar line. These elements are sufficient, however, to account for the line in laboratory spectra of silicon showing air lines.

Exner and Haschek's lines 3883·46, 4021·0 *and* 4764·20.—These lines do not appear in the Cape photographs. Neither Lockyer nor Eberhard finds them and M. A. de Gramont does not mention them. They also should be struck out from the list of silicon lines, as due to accidental impurities.

Line λ 4030.—Similarly with line λ 4030, found both by Exner and Haschek and Lockyer, although Lockyer states that it may be due to an

* 'Catalogue of 470 of the Brighter Stars' (1902), p. 52.

† 'Astrophysical Journal,' vol. 19, p. 272.

impurity, and he does not include it in any of his four groups. This line is not obtained either by Eberhard or myself, and should also be struck out.

Lines λ 3854 *and* λ 4103.—The lines 3853·9 and 4103·2 of Lockyer, which Eberhard does not obtain, are present in the Cape photographs, whilst Exner and Haschek record them as double lines. I do not doubt the silicon origin of these lines, but find them to be single and not double. The latter line is involved with both fluorine and oxygen lines when the spectra of those elements are present, but it is seen both in the spectra of the chloride and fluoride of silicon when examined under conditions which preclude the presence of the halogen spectra.

Mention may also be made of two pairs of silicon lines, one in the orange and another in the red, which were first noted by A. de Gramont. These I have confirmed, as well as the green pair also noted by A. de Gramont and confirmed by Lockyer.

New pair of Silicon Lines.—There is, however, another pair of lines which have not hitherto been recorded, which I regard as low-temperature silicon lines. Their wave-lengths are λ 4191·0 and λ 4198·5; they are well shown in strip IV. On the same negative are six other low-temperature lines, viz.: λ 3854, λ 3856, λ 3863, λ 3906 and the green pair λ 5042 and λ 5057. The pair λ 4128 and λ 4131 is very strong in the photograph (strip IV) whilst λ 4103 is a weak line.

The banded spectrum of the undecomposed fluoride is also well shown. This *partial* dissociation of the gas is evidence of the low-temperature condition, and the absence of the fluorine lines is well marked.

This new pair of lines was also obtained in the chloride, both in capillary tubes, at pressures of from 3·5 to 12·5 mm., and also in the spark between platinum electrodes in a bulb filled with the vapour of the chloride at atmospheric pressure.

Note on the Spectrum of Fluorine.

It is a remarkable fact that none of the observers who have worked with the spectrum of silicon tetra-fluoride have attempted to assign a definite spectrum to fluorine, although its lines must have accompanied most of their silicon spectra. It is also remarkable that Lockyer and Baxandall's Plate 11, strip A, shows the strongest fluorine lines clearly differentiated from the oxygen and silicon lines by being thickened in the lower half of the strip. Notice particularly the line beneath the letter V in Vacuum Tube.

None of the silicon and oxygen lines have this appearance, and the following

lines may be picked out in their photograph by mere inspection, viz.: λ 4103 λ 4109, λ 4246, λ 4299, and λ 4447.

The further elucidation of this interesting spectrum is suggested as a fruitful field for further research, which might preferably be undertaken outside an astronomical observatory.

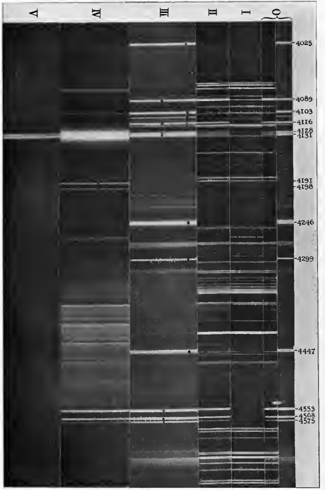
It is evident that a complete knowledge of the spectrum of fluorine will help to increase our knowledge of the spectrum of silicon, and probably that of other elements which have volatile fluorides.

There is a fluorine line on the green side of the 4116 silicon line with a wave-length of ±λ 4116·8, stronger than the fluorine line 4113 and fainter than 4119, which in spectra of dissociated silicon tetra-fluoride gives the silicon line too high a value for wave-length, unless sufficient dispersion is employed to separate the two lines.

A list of lines which may be ascribed to fluorine is appended. There are other lines in this region which may be due either to silicon or fluorine, but further experiments are necessary before their origin can be determined satisfactorily.

Spectrum of Fluorine.

	λ.	Intensity.		λ.	Intensity.
1st Triplet	3847·3	3	Group of five lines	4103·6	10
	3850·2	2		4109·3	5
	3851·8	1		4113·0	2
2nd Triplet	3899·0	2		4116·8	2
	3902·1	1		4119·3	3
	3904·0	< 1		4246·5	30
	4025·3	10 du ?		4299·3	7
	4084·1	2		4446·8	20


V
IV
III
II
I
O
4025
4089
4103
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4128
4131
4191
4198
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4447
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4568
4575